

IN THE SPECIFICATION

Please replace the paragraph beginning at page 1, line 9, with the following rewritten paragraph:

As one of the causes that a dislocation is formed in silicon single crystal in the pulling method, it has been known that cristobalite formed on the inside surface of the quartz glass crucible is released into the molten silicon. As a countermeasure to this, a process is known in which an alkaline earth metal is coated on an inside surface of the crucible to act as a crystallization ~~aceelerator~~ promoter. The metal forms a cristobalite layer on the inside surface of the crucible at an early stage of pulling ~~tip up~~ (e.g. U.S. Patent No. 5,976,247, Japanese Patent No. 3,100,836). In these inventions, a barium hydroxide solution is coated on the surface of the quartz glass crucible and the coated barium hydroxide reacts with carbon dioxide in air to form barium carbonate on the surface of the crucible. The barium carbonate is weakly adhered on the surface of the crucible by drying and is used as a crystallization ~~aceelerator~~ promoter.

Please replace the paragraph beginning at page 1, line 19, through page 2, line 12, with the following rewritten paragraph:

However, quartz glass crucibles surface-treated by conventional methods have the following problems and improvements are desired. That is, (A) since the barium carbonate powder on the quartz glass crucible is not fixed with any binder, the adhesion strength of the powder is very weak so that the powder is easily abraded and falls off when contacted by persons and instruments. Such abrasion occurs in the production process of the crucibles, such as product inspection, conveyance, and insertion to a carrying case, etc. It also occurs in the user's process, where the quartz glass crucible is set on a carbon susceptor in the ~~pulling up-equipment~~ crystal puller. As a result, its adhesion state becomes non-uniform and spot-

like. Furthermore, there is also a possibility that worker health is negatively affected because barium carbonate powder is scattered when the carrying case is opened. (B) Since the adhesion strength of powder is very weak, nucleation efficiency as a crystallization ~~accelerator- promoter~~ is low, and so the amount of barium carbonate required becomes excessive. (C) If the crucible is washed, the barium carbonate powder adhered on the surface of the crucible is washed away. It is then impossible to wash the crucible after the adhesion of the barium carbonate powder, even if some ~~soils~~ contaminants adhere on the surface of the crucible.

Please replace the paragraph beginning at page 2, line 20, through page 3, line 1, with the following rewritten paragraph:

[1] A surface modification process of a quartz glass crucible, the process comprising, coating a mixed solution, (hereinafter referred to as the silica sol liquid), containing a metal salt and a partial hydrolyzate of alkoxysilane oligomer on the surface of the crucible, ~~burning baking~~ said coated solution to form a transparent coated layer containing a crystallization ~~accelerator- promoter~~ derived from the metal salt in the silica matrix.

Please replace the paragraph beginning at page 3, line 7, with the following rewritten paragraph:

[3] The surface modification process of a quartz glass crucible, the process comprising, coating the silica sol liquid on the whole or a part of the inside and / or outside of the surface of the quartz glass crucible, and ~~burning baking~~ said coated silica sol liquid.

Please replace the paragraph beginning at page 3, line 13, with the following rewritten paragraph:

[5] The surface modification process of the quartz glass crucible, the process also comprising, drying the silica sol liquid, and ~~burning baking~~ said dried liquid at 350 to 1200°C for 10 to 120 minutes.

Please replace the paragraph beginning at page 3, line 17, with the following rewritten paragraph:

[6] A quartz glass crucible, having a transparent coated layer, in which the crystallization ~~accelerator promoter~~ is dispersed in the silica matrix, on the whole or a part of the inside and/or outside surface of the crucible.

Please replace the paragraph beginning at page 3, line 21, through page 4, line 1, with the following rewritten paragraph:

[7] The quartz glass crucible, wherein the crucible is made by, coating the silica sol liquid containing the metal salt and the partial hydrolyzate of alkoxy silane oligomer on the surface of the crucible, and ~~burning baking~~ the coated silica sol liquid to form a transparent coated layer containing the crystallization ~~accelerator promoter~~ derived from the metal salt in the silica matrix.

Please replace the paragraph beginning at page 4, line 2, with the following rewritten paragraph:

[8] The quartz glass crucible, wherein the crucible is made by coating the silica sol liquid containing a metal organic acid salt or a metal carbonate of one or more kinds of magnesium, calcium, strontium, or barium, on the surface of the crucible, and ~~burning baking~~ coated silica sol liquid to form the transparent coated layer containing the metal oxide or the metal carbonate as the crystallization ~~accelerator promoter~~.

Please replace the paragraph beginning at page 4, line 7, with the following rewritten paragraph:

[9] The quartz glass crucible used as the crucible for ~~pulling up~~ silicon single crystal production.

Please replace the paragraph beginning at page 4, line 8, with the following rewritten paragraph:

The surface modified quartz glass crucible of the present invention has a hard and transparent coated layer, in which the metal oxide or the metal carbonate is dispersed in a silica matrix, on the whole or a part of the inside and/or outside surface of the crucible. In addition, the metal oxide or metal carbonate acts as a crystallization ~~accelerator promoter~~ to the surface glass layer of the crucible at the high temperature of pulling up the silicon single crystal. Therefore, when the crucible is used for ~~pulling up the production of~~ silicon single crystal, a uniform cristobalite layer is formed on the inside surface of the crucible at an early stage of pulling up, and as a result a high dislocation free ratio of the pulled crystal can be obtained. Moreover, the strength of the crucible under a high temperature is increased by the uniform cristobalite layer formed on the inside or outside surface of the crucible.

Please replace the paragraph beginning at page 4, line 18, through page 5, line 7, with the following rewritten paragraph:

Moreover, since the coated layer is ~~integrated structurally to baked~~ on the surface of the crucible ~~by baking~~, it is very stable and has high durability. Therefore, there is no abrasion when contacted with instruments or persons and no problem that the adhesion state of the metal oxide in the coated layer becomes non-uniform. In addition, ~~the dislocation free ratio of silicon can be increased, since a uniform cristobalite layer is formed on the~~

~~surface of the crucible at pulling up the single crystal even if the coating layer is comparatively thin, the surface of the crucible is crystallized uniformly during pulling up the single crystal and the dislocation free ratio of silicon can be increased.~~ On the other hand, regarding the conventional quartz glass crucible having the adhered barium carbonate powder on its surface, since the adhesion strength of the barium carbonate powder is very weak, it can be washed away easily by acid washing. Therefore, it is impossible to wash the crucible even if ~~impurities some contaminants~~ are adhered on the surface of the crucible. While regarding the surface modified quartz glass crucible of the present invention, since the coated layer is baked on the surface of the crucible, it is not washed away by acid washing.

~~Impurities Contaminants~~ on the surface of the crucible can be removed easily by acid washing ~~to prevent the contamination of the silicon single crystal by such impurities to great an extent as possible.~~

Please replace the paragraph beginning at page 5, line 11, with the following rewritten paragraph:

The surface modification process for producing the quartz glass crucible of the present invention is a formation process for a transparent coated layer on a surface of a crucible, where a crystallization ~~accelerator promoter~~ is dispersed in a silica matrix. Moreover, the quartz glass crucible of the present invention has a transparent coated layer on the whole or a part of the inside and / or outside surface of the crucible. The crystallization ~~accelerator promoter~~ is a metal compound except for silica, which is for example a metal oxide or metal carbonate. Concretely, the metal is for example, magnesium, calcium, strontium, or barium etc.

Please replace the paragraph beginning at page 5, line 18, with the following rewritten paragraph:

The transparent coated layer, where the crystallization ~~accelerator promoter~~ is dispersed in the silica matrix, can be formed by coating the mixed solution (the silica sol liquid) containing the metal salt and the partial hydrolyzate of alkoxy silane oligomer on the surface of the crucible, and by ~~burning baking~~ this coated silica sol liquid.

Please replace the paragraph beginning at page 5, line 22, through page 6, line 5, with the following rewritten paragraph:

The silica sol liquid forming the transparent coated layer is a mixed solution which contains both a metal salt and a partial hydrolyzate of an alkoxy silane oligomer as components. The metal salt is for example a salt of magnesium, calcium, strontium, or barium, which is a useful metal as a crystallization ~~accelerator promoter~~ to ~~accelerate promote~~ the formation of the cristobalite layer on the surface of the quartz glass crucible. In addition, a silica sol liquid containing a stabilizing reagent can also be used. The preferred metal salt is a metal organic acid salt or a metal carbonate.

Please replace the paragraph beginning at page 6, line 6, with the following rewritten paragraph:

The most preferable metal organic acid salts are carboxylates. As an acyloxy group to form the carboxylate, the materials indicated by the general formula $C_nH_{2n+1}COO$, where n is an integer of 3 to 7, are preferable. Concretely, the acyloxy group derived from n-butyric acid, α -methyl butyric acid, ~~iso-valeric~~ iso-valeric acid, 2-ethyl butyric acid, 2,2-dimethyl butyric acid, 3,3-dimethyl butyric acid, 2,3-dimethyl butyric acid, 3-methyl pentanoic-acid, 4-methyl pentanoic acid, 2-ethyl pentanoic acid, 3-ethyl pentanoic acid, 2,2-dimethyl pentanoic acid, 3,3-dimethyl pentanoic acid, 2,3-dimethyl pentanoic acid, 2-ethyl hexanoic acid, or 3-ethyl hexanoic acid, etc., can be used suitably.

Please replace the paragraph beginning at page 7, line 3, with the following rewritten paragraph:

As another example of a usable solvent, a ketone, such as acetone, methylethylketone, and methyisobutylketone, and a hydrocarbon, such as toluene, xylene, hexane, and cyclohexane, can be used. It is possible that a mixture of two and more kinds of these organic solvents is used. The solution containing a carboxylate of a metal is mixed with the solution containing the partial hydrolyzate of an alkoxy silane oligomer, to provide the predetermined composition, and the silica sol liquid is prepared. The silica sol liquid has high wettability to the surface of the crucible. The final hard and transparent silica coated layer, in which the metal oxide is dispersed in the silica matrix, can, be formed by ~~burning baking~~ to dehydrate said silica sol liquid after the organic components are removed completely.

Please replace the paragraph beginning at page 7, line 12, with the following rewritten paragraph:

The partial hydrolyzate of an alkoxy silane oligomer used in the present invention is obtained by a process in which the alkoxy silane oligomer is hydrolyzed under the controlled reaction conditions, and after the alcohol is removed, each generated OH group is bonded together to form the silica sol. As a suitable starting material, one or more silane compounds having at least one, preferably more than two, and more preferably more than three alkoxy groups, can be used. Concretely, tetraethoxysilane (= ethylsilicate), tetrapropoxysilane, methyltriethoxysilane, dimethylmethoxysilane, phenyltriethoxysilane, chlorotrimethylsilane, various kinds of silane coupling reagents, such as vinyltriethoxysilane, $\gamma\gamma$ -

aminopropyltriethoxysilane, etc., also can be mentioned. Ethylsilicate, which is the cheapest and to be easily hydrolyzed, is preferred.

Please replace the paragraph beginning at page 8, line 8, with the following rewritten paragraph:

Regarding the metal amount in said silica sol liquid, it is preferable that the metal amount in the coated layer is 1×10^{-9} to 1×10^{-6} mol/cm², ~~per unit area~~, which is calculated as an oxide, when the coated silica sol liquid is baked to form said coated layer on the surface of the crucible. For example, it is preferable that the metal content of the silica sol liquid is 0.01 to 15 weight %, preferably 0.5 to 10 weight %, which is calculated as an oxide, and the silicon concentration is 0.5 to 30 weight %, which is calculated as SiO₂. The solution containing the metal salt and the partial hydrolyzate solution of alkoxy silane oligomer, are mixed and prepared to provide the preferable metal content and silicon concentration. When the metal content is less than 0.01 weight %, which is calculated as an oxide, a repeat coating is necessary ~~to nucleate the crystal sufficiently on the surface of the crucible~~ to form the desired devitrification layer thickness on the surface of the crucible. On the other hand, when the content is more than 15 weight %, it is difficult to make a stable mixed solution. Moreover, when the silicon concentration is less than 0.5 weight %, which is calculated as SiO₂, the strength of the formed coated layer is not sufficient, and when the concentration is more than 30 weight %, it is difficult to make the mixed solution stable. It is preferable that the silicon concentration is 0.5 to 30 weight %, more preferably 1 to 20 weight %.

Please replace the paragraph beginning at page 8, line 24, to page 9, line 7, with the following rewritten paragraph:

As the method for coating the silica sol liquid on the surface of the crucible a spray method and a dipping method, etc. can be used, and the coating method is not limited. In addition, the silica sol liquid on the surface of the crucible can be coated on a part or the whole of the inside surface or can be on a part or the whole of the outside surface; or can be on a part or the whole of both inside and outside surfaces. In order to increase the dislocation free ratio of the single crystal ~~by the crystallization acceleration effect with the metal oxide crystallizing the inside surface of the crucible during pulling up of the crystal,~~ the silica sol liquid must be coated on at least the whole or a part of the inside surface of the crucible.

Please replace the paragraph beginning at page 9, line 8, with the following rewritten paragraph:

The silica sol liquid is coated on the surface of the crucible and is burned baked. It is suitable that the burning baking temperature is 350 to 1200°C, preferably 600 to 1000°C, and the burning baking time is 10 to 120 minutes. When the burning baking temperature is less than 350°C, the strength of the coated layer is not sufficient, and when said temperature is more than 1200°C, there is a possibility that the coated layer is denitrified devitrified. By this burning baking, the silica component of the silica sol liquid forms the hard silica matrix. Moreover, regarding the silica sol liquid containing the metal organic acid salt as the metal salt, the metal organic acid salt is decomposed into the metal oxide and the transparent coated layer in which the metal oxide is uniformly dispersed in the silica matrix, is formed on the surface of the crucible. ~~Burning includes heating and/or oxidation and does not require that combustion of an organic component take place.~~

Please replace the paragraph beginning at page 9, line 19, through page 10, line 3, with the following rewritten paragraph:

On the other hand, regarding the quartz glass crucible containing the metal carbonate, when the burning baking temperature is more than the decomposition temperature of the metal carbonate, the coated layer, where the metal carbonate is decomposed to the metal oxide to disperse in the silica matrix, is formed. On the other hand when the burning baking temperature is less than the decomposition temperature, the coated layer, where the metal carbonate is dispersed in the silica matrix a metal carbonate, is formed. In addition, when the burning baking temperature is near the decomposition temperature of the metal carbonate, the coated layer, where the metal oxide decomposed from a part of the metal carbonate and the non-decomposed metal carbonate are mixed, can be formed.

Please replace the paragraph beginning at page 10, line 5, with the following rewritten paragraph:

Preparation of a partial hydrolyzate of alkoxy silane oligomer

~~Preparation of a partial hydrolyzate of an alkoxy silane oligomer.~~ Two kinds of a partial hydrolyzate of alkoxy silane oligomer of (I) and (II) were prepared at the mixing ratios of raw materials and the reaction conditions, shown in Table 1.

Please replace the paragraph beginning at page 11, line 1, with the following rewritten paragraph:

(2-3) 0.5g of barium carbonate powder having an average particle size of 1 μm 10 μm was dispersed in 100g of a partial hydrolyzate of alkoxy silane oligomer shown in Table 1 (I) to prepare the silica sol liquid F in Table 2. In the reaction vessel for the preparation, the

equipment having the stirring propeller was used to prevent the precipitation of the barium carbonate powder.

Please replace the paragraph beginning at page 11, line 8, with the following rewritten paragraph:

Five kinds of the silica sol liquids, (A-E), shown in Table 2, were sprayed to coat the surfaces of quartz glass crucibles ~~for pulling up single crystal silicon production~~, and the single crystal, and the coated layers were formed by ~~burning baking~~ the coated liquids at 850°C for 30 minutes, wherein the crucibles were made by an arc fusion with rotating mold method, which is generally used in the process to produce the crucible for pulling up a single crystal.

Please replace the paragraph beginning at page 11, line 13, with the following rewritten paragraph:

In this case, the quartz glass crucibles were surface treated by using the liquids F and H. Sample No. 6 was made by spaying the silica sol liquid F to coat the surface of the crucible to be burned at 850°C for 30 minutes. In addition, Sample No. 8 was made by a conventional coating method. This is, the liquid H, where barium hydroxide octahydrate was mixed with water, in which the mixing ratio is 3g of barium hydroxide octahydrate in ~~1-~~
liter of water, was sprayed on the crucible to heat at 300°C with carbon dioxide gas.

Please replace the paragraph beginning at page 12, line 13, through page 13, line 4, with the following rewritten paragraph:

Washing tests were carried out on the quartz glass crucibles, (No. 1, 6, 8) in Table 2, which, were coating treated. The tests were conducted on the following processes. (1) Washing with pure water and drying. (2) Washing with pure water and drying after washing

with dilute hydrochloric acid. The adhesion amounts of the residual barium on the surface after each washing test, are shown in Table 3. Regarding the quartz glass crucible of the present invention (No. 1), barium was not removed, and the adhesion amounts were not changed in the water washing process (1) and the acid washing process (2). Moreover, regarding the quartz glass crucible of the present invention (No. 6), although the form of barium was the ~~sodium~~ barium carbonate, which was same as the conventional, one, since the barium carbonate was dispersed in the silica sol liquid and coated ~~to burn and baked~~, the coated silica became the preservation layer. So the barium was not removed in the washing process (1) and the acid washing process (2) like the quartz glass crucible (No. 1). On the other hand, regarding the conventional quartz glass crucible (No. 8), since the barium carbonate was not baked, the barium was washed away a little in the water washing process (1), and the barium carbonate was washed away completely in the acid washing process (2).

Please replace the paragraph beginning at page 13, line 7, through page 14, line 3, with the following rewritten paragraph:

The pulling up tests of the silicon single crystal were carried out by using quartz glass crucibles having transparent coated layers (No. 1 to No. 5), and the quartz glass crucible where the barium carbonate powder was dispersed in the partial hydrolyzate of the alkoxysilane oligomer (No. 6). The dislocation free ratios of the pulled crystals, are shown in Table 4. (The dislocation free ratio is defined as kilograms of dislocation free single crystal per kilograms of polysilicon charged to the crucible.) Moreover, for the comparison, the same pulling up tests were also conducted on quartz glass crucible (No. 7), in which the surface was not modified and there is no crystallization ~~accelerator~~ promoter layer on its surface and to the quartz glass crucible (No. 8), in which the crystallization ~~accelerator~~ promoter layer was formed by a conventional method. The dislocation free ratios of the

single crystal are shown in Table 4. In addition, the thickness of the crystallization layer of the crucible after pulling up the single crystal was measured. The thickness of the crystallization layers is shown in Table 4. As shown in the results in Table 4, regarding the quartz glass crucible of the present invention, the crystallization layers having the sufficient layer thickness were formed on the surface of the crucible also with comparatively a little amount of barium, and a high dislocation free ratio could be obtained. On the other hand, regarding the quartz glass crucible of the comparative example No. 7, the dislocation free ratio was remarkably low. Moreover, regarding the quartz glass crucible of the comparative example No. 8, where barium carbonate was adhered by the conventional method, although this quartz glass crucible has the almost same adhesion amount of barium as used of the present invention, the crystallization layer after pulling up the single crystal was thin in the crucible, and the dislocation free ratio was remarkably low.

Please replace the paragraph beginning at page 14, line 5, with the following rewritten paragraph:

[Burning] Baking temperature

Please replace the paragraph beginning at page 14, line 6, with the following rewritten paragraph:

The silica sol liquid (No. 1) shown in Table 2 was sprayed to coat the surface of a quartz glass crucible for pulling up the single crystal, and a coated layer was formed by baking said coated liquid at the temperatures shown in Table 5 for 30 minutes. The mechanical strength of the coated layer was evaluated according to the specification standard (JIS 5600-5-4). This evaluation was carried out using the scratching method with a marketed pencil (trade name Mitsubishi UNI). Furthermore, washing tests were also conducted. The

washing tests were carried out by measuring the adhesion amount of the residual barium on the surface after washing with pure water and drying. Moreover, for comparison, the same tests were conducted on a quartz glass crucible which was not ~~burned~~ baked after coating. These results are shown in Table 5.

Please replace the paragraph beginning at page 15, line 13, through page 16, line 5, with the following rewritten paragraph:

Regarding the quartz glass crucible having the coated layer of the present invention (No. 3), the crystal layer was formed uniformly on the inside surface of the crucible with the crystallization ~~accelerator~~ promoter contained in the coated layer, and the releasing of cristobalite ~~was stopped~~ did not occur. Therefore, even when the pulling up of a single crystal was repeated 4 times, a high dislocation free ratio, which was the level of 80%, was kept. As a result, the crucible life was prolonged. On the other hand, regarding the conventional quartz glass crucible having weakly adhered barium carbonate powder, (No. 8) in Table 2, the cristobalite was deposited non-uniformly and partially as the pulling up was repeated. Then, the frequency of the release of cristobalite to the molten silicon increases so that the dislocation free ratio was decreased gradually. In addition, regarding the crucible, in which the pulling up the single crystal was repeated 4 times, the cristobalite layer was not identified on the surface of the crucible. By the way, regarding the conventional quartz glass crucible having the adhered barium carbonate powder (No. 8), it is necessary that the amount of adhered barium is more than $20 \mu\text{m/g} \mu\text{g/cm}^2$ for obtaining the multi-pulling effect, which was the same as the present invention. When such an amount of barium is adhered on the surface of the crucible, it cannot be avoided to give the bad influence to the quality of the single crystal silicon.

Please replace the paragraph beginning at page 16, line 8, with the following rewritten paragraph:

2-ethylhexanoic acid salts of Mg, Ca, and Sr were added to the partial hydrolyzate of the alkoxy silane oligomer shown in Table 2 (I) to prepare a silica sol liquid. The silica sol liquid was sprayed to coat a quartz piece having 10 cm square, and the transparent coated layer was formed by burning baking said coated liquid at 850°C for 30 minutes. The adhesion amount of the metal was adjusted, so that it became 1 µg/cm², which was calculated as an oxide. Next, the transparent coated layer was put into an electric furnace to bake at 1450°C for 5 hours in argon gas at 1 atmosphere pressure. Then, it was confirmed that the uniform crystallization layer could be formed by also using all said metals.

Please replace the paragraph beginning at page 16, line 17, through page 17, line 5, with the following rewritten paragraph:

A quartz glass crucible has a transparent coated layer containing a crystallization accelerator promoter on the surface, and since the coated layer forms an integrated structure to the surface of the crucible, there is no abrasion, and the adhesion state of a crystallization accelerator promoter, such as barium, contained in the coated layer, is kept uniformly. Therefore, the cristobalite formation on the surface of the crucible ~~at the~~ during pulling up the single crystal is completely uniform, so that an excellent dislocation free ratio can be obtained. Moreover, there is no problem that the coated layer is abraded in contact with the handling instruments or persons, in the working process after making the crucible, during from the inspection to the shipment, and the working process in the user side of the crucible. In addition, there is no conventional problem that the fine barium carbonate powder is scattered whenever the case containing the crucible is opened.

Please replace Table 4 at page 19, with the following Table:

Table 4

No.	1	2	3	4	5	6	7	8
<u>Rates of Single Crystallization Dislocation free ratio %</u>	81	83	85	83	80	81	35	55
Crystallization Layers After Pulling up μm	80	77	83	95	90	103	0	10

Please replace Table 5 at page 19 with the following Table:

Table 5

<u>Burning Baking Temperature</u>	<u>Non-Baking Not-Baked</u>	200°C	400°C	600°C	800°C	1000°C
Hardness of Coating Layer	Cracking Appeared by 2B	Cracking Appeared by 3H	No Cracking by 5H	No Cracking By 6H		
Washing Test Ba Amounts Before Washing Ba Amounts After Washing and Drying	0.6 0	0.6 0.2	0.6 0.5	0.6 0.6		

(Note) Ba Amounts is $\mu\text{g} / \text{cm}^2$

Please replace Table 6 at page 20 with the following Table:

Table 6

Rates of Single Crystallization Dislocation free ratio %

Number of Times of Pulling up	1	2	3	4
Coated Crucible (No. 3)	85	85	83	83
Conventional Crucible Having Ba Carbonate Powder (No. 8)	55	50	47	42